6.0 REVIEW OF PREVIOUS INCIDENTS

The following incidents involved the former chlorination system for the Hanford 300-Area Water Treatment Facility. Information about these incidents was obtained from the U.S. Department of Energy (DOE) Occurrence Reporting and Processing System (ORPS). Where relevant, these incidents were considered during the hazard and operability (HAZOP) study for the new system.

- 10/9/92 **Leak Detector Failure The** leak detector was outside of specified tolerances, as required in the maintenance procedure. Plant operations personnel were notified. Replacement parts were not available, and the maintenance craftsman removed the device from service until parts could be obtained the next day. During the swing and the following day shift, personnel did not know the detector had been removed from service. A "conduct of operations" review of the day's activities was held with **all** on-coming and off-going **staff**. This leak detector had experienced recurring failures and was replaced. (See Scenario 5-2 in the HAZOP study worksheets, Appendix B.)
- 11/19/92 Chlorine Leak The chlorine detector in the chlorination room alarmed in the afternoon, indicating that one of the chlorinators was leaking. Facility operations personnel were evacuated, and the Hanford Fire Department Emergency Response Team was notified. The system was shut down, the in-service chlorinator was isolated, and the standby chlorinator was put into service. No one was injured, and only a minimal amount of chlorine was released. The chlorine was generally confined to the chlorination room. It was determined that the #1 chlorinator injector system had developed a leak. The system tiled because of imperfections within gasket material. The failed material was replaced. (See Scenarios 1-4, 1-10, and 4-9 in the HAZOP study worksheets, Appendix B.)
- 11/21/92 Chlorine Leak A chlorine alarm was received, the Hanford Fire Department was notified, and the Hanford Hazardous Materials (HAZMAT) Team was dispatched. The Hanford 300-Area Water Treatment Facility was shut down. A tie-in line was put into service to supply water to the Hanford 300-Area from the City of Richland after Richland was notified. Failed internal parts of the #2 chlorinator and a system isolation valve packing gland were leaking. A weak spring in a chlorinator pressure-regulating valve caused a rubber diaphragm to fail. There were no injuries, and the minimal amount of chlorine released was generally confined to the chlorination room. The spring and diaphragm were replaced. The isolation valve was repacked. (See Scenarios 1-10 and 1-4 in the HAZOP study worksheets, Appendix B.)
- 1/4/93 Chlorine Leak Detector Alarm While performing routine equipment changes, the onduty operator noticed a chlorine odor in the chlorination room. After the operator exited, the chlorine leak detector in the building alarmed. The plant operator evacuated the Water Treatment Facility, and the Hanford HAZMAT

Team responded and isolated the system. The Water Treatment Facility was shut down, and the City of **Richland** water supply was **placed** in service. There were no injuries from the occurrence.

During maintenance activity, the operator had isolated and drained the in-service chlorinator according to procedures in effect at the time. These procedures did not allow sufficient time for evacuating the chlorine ejector prior to draining the chlorinator. The system was checked for leaks, but no leaks were found. The procedure was revised to allow sufficient time to evacuate the system. With different procedures now in place, this incident has consequences similar to Scenario 1-11 in the HAZOP study worksheets (see Appendix B).

• 1/16/93 Chlorine Leak **Detection Alarm** — A chlorine high-level alarm occurred. The Hanford Fire Department was notified, and several surrounding buildings were evacuated. Testing by the Hanford HAZMAT Team found no detectable chlorine in the air. Fewer than two hours later, the "all clear" was given. It was determined that the detector provided a **false** alarm. Tests performed by an instrument technician, however, showed that the detector was operating within the manufacturer's recommended tolerances. No leaks were identified when the system was restored to operation.

Prior to the occurrence, re-liquefaction of the gaseous chlorine within the chlorination room piping had been occurring. An additional heat source had been provided to **rectify** the problem. The heater had been placed next to the leak detector. The detector's electronics were **affected** by the increased room temperature. A voltage spike was created within the instrument and resulted in the **false** alarm. (See Scenarios 5-2 and 2-5 in the HAZOP study worksheets, Appendix B, and recommendation #4 in Section 4.0.)

7.0 IDENTIFIED HAZARDS

Chlorine has been used for many years to treat water on the Hanford Site. Westinghouse Hanford Company uses the Chlorine *Manual* (The Chlorine Institute, 1986, 5th edition), *Operating Procedure: Chlorine Cylinder Handling and Storage* (Westinghouse Hanford Company, no date), and the *Material Safety Data Sheet* (MSDS) (Occupational Health Services, Inc., 1993; see Appendix D) as references for chlorine handling.

7.1 Properties of Chlorine

Chlorine is a dense, nonflammable, greenish-yellow gas with a **bleach-like** choking odor. It is **2.5** times heavier than air. Liquid chlorine is a clear amber color and is 1.5 times heavier than water. Chlorine is generally shipped as a compressed, **liquified** gas with a vapor pressure of **85.5** psig at **70°F**. In both gaseous and liquid states, chlorine is nonflammable and nonexplosive. However, like oxygen, it is capable of supporting the combustion of substances such as hydrogen, ammonia, fuel gases, ether, turpentine, and most hydrocarbons. Finely divided metals and organic matter may react violently with chlorine. Steel and iron ignite and bum in an atmosphere of chlorine at about **484°F**. Chlorine reacts with water to form corrosive solutions of hydrochloric and **hypochlorous** acid.

7.2 Physiological **Effects**

Chlorine is corrosive, highly toxic, and severely irritating to all living tissue. Exposure may cause skin bums, permanent eye damage, and damage to the respiratory system. Inhalation exposure to higher **concentrations** of chlorine may be fatal. Airborne concentrations of chlorine above 3 to 5 parts per million **(ppm)** by volume are readily detectable by a normal person. In higher concentrations, the irritating effect of chlorine makes it unlikely that any person would willingly remain in a chlorine-contaminated atmosphere.

Persons exposed to airborne concentrations of chlorine greater than 15 ppm generally experience difficulty in breathing. Excessive or prolonged exposure causes pulmonary edema and death. The physiological effects of various concentrations of chlorine gas **are** shown in Table 2 along with the limits for chlorine exposure in the workplace. Appendix C includes graphs that estimate the areas affected by various chlorine release scenarios. Exposure to chlorine produces no known cumulative effects.

Table 2. Physiological Responses and Exposure Limits for Chlorine Gas Concentrations

Effects/Emits	Parts per Million (ppm) by Volume
Threshold limit value ^(a)	0.5
Least detectable odor ^(b)	3.5
Least amount required to cause irritation of throat(b)	15
Immediately Dangerous to Life or Health (IDLH) concentration(c)	30
Dangerous for short exposures ^(b)	50
Fatal for brief exposures ^(b)	1,000

⁽a) American Conference of Governmental Industrial Hygienists, 1992.

⁽b) Sax, et al., 1979.

⁽c) National Institute for Occupational safety and Health, 1990.

8.0 ANALYSIS METHOD

The analysis method used in this example process hazard analysis (PrHA) was the hazard and operability (HAZOP) study. The HAZOP study was developed specifically for process industries to identify both safety hazards and operability problems that could compromise a plant's ability to achieve design productivity.

The basic concept behind HAZOP studies is that processes work well when operating under design conditions, and that deviations from process design conditions cause hazards and **lead** to operability problems. In a HAZOP study, guide words are used to assist an analysis team in considering the causes and consequences of deviations from design conditions. The guide words are applied at specific points or "nodes" in a process and are combined with process parameters to identify potential deviations.

The HAZOP study method entails analyzing hazardous events (accidents) to see how they may occur and what undesired consequences are possible. Each sequence of failures and conditions leading to an accident event is a unique scenario. Every accident scenario includes an *initiating event* or cause (e.g., mechanical or human failure), a process deviation(s), an accidental event or consequence, and an impact (injuries and/or damage). Protection may be employed to keep the accident from occurring. Mitigation may reduce the severity of the impact (see Figure 9).

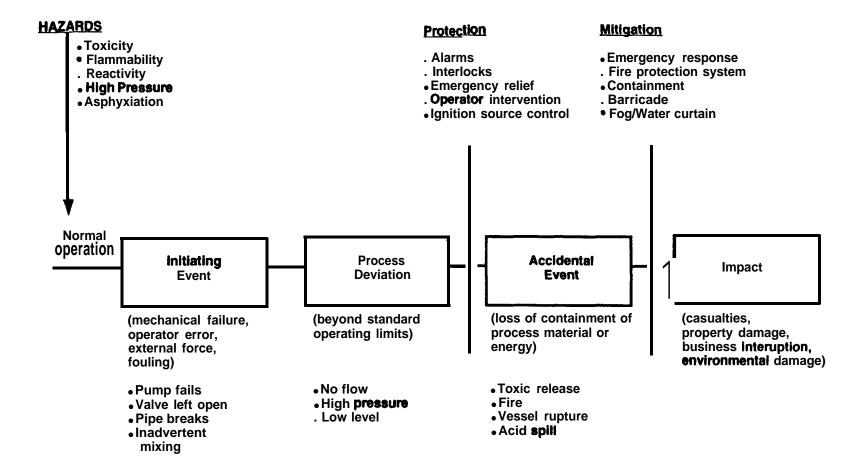
The HAZOP methodology

- Postulates deviations from design intent
- Examines the causes of the deviations
- Determines the consequences and range of potential impacts if deviations are allowed to continue uncorrected
- Assesses the protection included in the system design to reduce the likelihood of the cause and/or to prevent or minimize the consequences or impacts.

A HAZOP study requires considerable knowledge of the process being studied, its instrumentation, and its operation. This information is usually provided by team members who are experts in these areas. Where weaknesses or safety improvements in the design or operating procedures are identified, the HAZOP study team develops a list of action items to be further addressed.

Based on the level of complexity and the general nature of the chlorination process at the Hanford 300-Area, the HAZOP study is an appropriate PrHA method to analyze the hazards of the operation.

For a more detailed description of the HAZOP study method and other PrHA methods, see the *DOE Guideline: Guide For Chemical Process Hazard Analysis* (*Draft*, **DOE/EH**, March 1993) and the *Guideline for Hazard Evaluation Procedures* (Center for Chemical Process Safety, 1992, 2nd edition).



9.0 ANALYSIS TEAM

The hazard and operability (HAZOP) study team consisted of the team leader, Mr. Fred Leverenz, from Battelle's Process Safety and Risk Management Group; Westinghouse Hanford Comparty (WHC) personnel; representatives from the U.S. Department of Energy (DOE) Headquarters and Richland Operations Office; and personnel from the Pacific Northwest Laboratory (PNL) Training Group and Risk and Safety Analysis Group.

Table 3 lists the personnel who participated in the 4-day HAZOP study. Appendix E contains the resumes of the HAZOP study team.

Table 3. HAZOP Study Team Members

PARTICIPANT	ORGANIZATION	ROLE
Fred Leverenz	Battelle-Columbus	PrHA Expert and Team Leader
Karl Agee*	Westinghouse Hanford Company	Team Member
Joe Angyus	Pacific Northwest Laboratory	Team Member
Samuel Camp, Jr.	Westinghouse Hanford Company	Process Operator and Team Member
Rudy Hansen	Pacific Northwest Laboratory	scribe
Sanji Kanth [*]	DOE Headquarters	Team Member
Ken Murphy*	DOE Headquarters	Team Member
Dickie Ortiz	DOE Richland Operations Office	Team Member
Pete Pelto*	Pacific Northwest Laboratory	Team Member
John Piatt*	Pacific Northwest Laboratory	Team Member
Jay Rude	Westinghouse Hanford Company	Process Engineer and Team Member

^{*} Partial attendance

10.0 FACILITY SITING ANALYSIS

As part of the process hazard analysis (PrHA), a walkdown of the Hanford 300-Area Water Treatment Facility was performed on May 22, 1993. The following is a description of the general layout of the facility.

The Hanford 300-Area Water Treatment Facility is located within the **fences** of the Hanford 300-Area and away from offsite populations. Most **near-by** human activities are related to facility operations and/or chlorine delivery and associated crane manipulations.

The Columbia River is directly east of the Water Treatment Facility. The closest residences are isolated houses on the opposite side of the river, more than **three-quarters** of a mile away. A pump house is located east of the **facility** near the river. The east **access** road, which supports only **low** levels of traffic, is more than 120 feet away, at a lower elevation.

The chlorination room (80 square **feet**) and the chlorine cylinder storage area (300 square **feet**) are on the north side of the 315 Building. The building closest to the chlorination process is the 338 Maintenance Shop. It is more than 60 feet to the west of the chlorination room. This building is being transferred from the Westinghouse Hanford Company **(WHC)** to Kaiser Engineers, Inc., to be used as a **fabrication** shop. About 20 to 40 employees will eventually occupy the building.

Other buildings in the vicinity of the chlorination process are the 337 Office Building (325 employees), which is more than 200 feet to the south, and the 3768 Modular Office Building (15 employees), which is more than 150 feet to the north. To the north of the 3768 Building are the 3769 Modular Office Building (15 employees), the M103 trailer (7 employees), the M105 trailer (9 employees), and the 3770 Modular Office Building (15 employees). All buildings have multiple exits and emergency plans. The emergency plan evacuation route for the 337 Office Building is toward the south, away from the chlorination process. The emergency plan addresses leaks and spills, as well as unusual, irritating, or strong odors.

The regulator for the chlorine cylinders vents near the roof level of the chlorine cylinder storage area. ShutOffs (G 1 and G2) for the chlorine **feed** are inside the storage area. See Appendix C for potential impacts of chlorine releases.

11.0 HUMAN FACTORS

The Occupational Safety and Health Administrative (OSHA) rule on process safety management (the PSM Rule) requires the inclusion of human factors in process hazard analyses (PrHAs). Human factors may positively or negatively influence the likelihood of an operator making an error when interacting with a process. For example, if an operator is required to change the position of a valve, but the location of the valve is not specified and/or the valve is not labeled, the operator may have difficulty responding correctly. More positively, if an operator has enough time to complete an action such that he/she can verify the action, then it is more likely that the operator will act correctly.

Human **factors** are included in this hazard and operability **(HAZOP)** study by adding notations in the **CAUSE** or **PROTECTION** column of the HAZOP study worksheets (see Appendix B) immediately after a human error is indicated. The notation used is "—I-IF" for human factors that may negatively influence an operator's performance and "+HF" for human factors that may help an operator to act correctly.

In some places in the HAZOP study worksheets, human interactions/errors are indicated, but no notation is present. If no human **factors** notifications are present, the HAZOP study team judged that the human factors components of that scenario were "normal," expected good practice. For example, the HAZOP study team assumed that **all** equipment **was** labeled.

Table 4 provides a generic checklist for human factors. This list is recommended for use by PrHA teams to help recognize the human factors that influence each accident scenario.

Table 4. Human Factors Checklist

FACTORS	EXPECTED (+)	NEGATIVE (-)
DISPLAYS/CONTROLS	Essy to read/understand	Hard to read/understand/interpret
	Controls accessible	Controls inaccessible
	Display identifies related device	Display does not show device
	Alarms discriminable, relevant	Alarms confusing, irrelevant
	Display mimics action/position	Display is not representational
	Immediate feedback	No immediate feedback
EQUIPMENT	Clearly labeled	Not labeled or mislabeled
	Accessible	Not easily accessed
	Easily operated	Difficult to operate/change position
	Components easy to distinguish	Several components look similar
PROCEDURES	Realistic; reflect the way things are done	Unrealistic; not the way things are done
	Location of devices/action provided	No location of devices/action provided
	Allows unambiguous determination of event in progress	Results in inappropriate diagnosis
	Clear, consistent format	Confused, difficult to read
	Complete and accurate	Missing step in procedure or wrong sequence
COMPETENCE	Operators generally well trained in related procedures	Operators not well trained in related procedures
	Operators have considerable experience	Operators are novices
	Peer review used in certification	No peer review in certification
	Operators given periodic feedback on performance	No feedback
	Design changes are appropriately reviewed	Design changes performed without adequate review

Table 4. Human Factors Checklist (Continued)

FACTORS	EXPECTED (+)	NEGATIVE (-)
STRESS	Adequate time available to complete action	Too little time available to complete action
	Shift assignments are permanent, or shift changes do not create time confusion	Shift changes often occur in the middle of the week; double shifts often occur
	Staffing is at an appropriate level	Staff are needed, or some shifts are intentionally short-staffed
	Safety is emphasized	Operators are concerned about 10ss of production if plant inadvertently shut down for safety issue
	Accountabilities are well defined	Accountabilities are poorly defined
	operator performs acceptable number of tasks	Operator must conduct diverse operations within same time period
ENVIRONMENT/ WORKPLACE	Sufficient lighting	Inadequate lighting
	Minimal noise level	High noise level
	Moderate weather	Extreme weather conditions
	Comfortable temperature/humidity	Extreme temperature/humidity
	Low vibration environment	High vibration environment
	Good job aids	No memory support

12.0 SUMMARY

During the process hazard analysis (PrHA) of the chlorination process at the Hanford 300-Acre Water Treatment Facility, areas of uncertainty were identified. Twelve action items and recommendations were made by the PrHA team to clarify these uncertainties and to verify process conditions (see Section 4.0). These recommendations are being reviewed to determine whether further action is needed to improve the chlorination system. In addition, procedures were developed during the PrHA exercise to control and avoid potential hazards.

To comply with the Occupational Safety and **Health** Administration **(OSHA)** rule on process safety management (the PSM Rule), all of the PrHA findings and recommendations must be resolved and documented. All actions taken as a result of the PrHA findings must be reported to employees involved in the process and to any other affected individuals. In addition, the PrHA must be reviewed every 5 years to ensure that it is consistent with the current configuration and operation of the chlorination process. The PrHA, related updates, and the documented resolution of the recommendations must be maintained for the life of the process.

13.0 REFERENCES AND BIBLIOGRAPHY

American Conference of Governmental Industrial Hygienists. 1992-1993 *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, Cincinnati, OH, 1992.

Capital Controls Co. Inc. *Instruction Manual: Cabinet Mounted Gas Feeders*, *Manual/Automatic Control*, *Series 4000*, Bulletin B3. 84000.2, Colmar, PA, 1992.

Capital Controls Co. Inc. *Operation and Maintenance Manual for Westinghouse Hanford Company*, CCC# C722730. Series of Bulletins A2.41 101.1, A2.62105.4, A2.60000.4, A2.41002.0, A2.41701.0, A2.41009.0, A2.41410.2, A1.14100.7, B3.84000.2, A1.11450.1, B3.71051.1, B3.7858.8, B3.7859.3, B3.7854.2, B3.7860.5, B3.71018.4, B3.71049.0, B3.7147.11, B3.7135.18, B3.7133.7, B3.7814.4, and B3.7193.11, Richland, WA, 1993.

Center for Chemical Process Safety. *Guidelines for Hazard Evaluation Procedures*, 2nd Edition, American Institute of Chemical Engineers, New York, NY, 1992.

The Chlorine Institute, Inc. *Chlorine Manual*, 5th Edition, Washington, DC, 1986.

The Chlorine Institute, Inc. *Pamphlet 17: Cylinder and Ton Container Procedure for Chlorine Packaging*, 2nd Edition, Washington, DC, 1993.

The Chlorine Institute, Inc. *Pamphlet 74: Estimating the Area Affected by a Chlorine Release*, 2nd Edition, Washington, DC, 1991.

Merck & Co., Inc. *The Merck Index, an Encyclopedia of Chemicals and Drugs,* 9th Edition, Rathway, NJ, 1976.

National Institute for Occupational Safety and Health. *NIOSH Pocket Guide to Chemical Hazards*, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, Cincinnati, OH, June 1990.

occupational Health Services, Inc. *Material Safety Data Sheet: Chlorine*, OHS-04600, New York, NY, 1993.

Sax, N. Irving, et al. *Dangerous Properties of Industrial Materials*, 5th Edition, Van Nostrand Reinhold, New York, NY, 1979.

U.S. Code of Federal Regulations. *Process Safety Management of Highly Hazardous Chemicals*, 29 <u>CFR</u> 1910.119, Occupational Safety and Health Administration, Washington, DC, 1992.

U.S. Department of Energy. *DOE Guideline: Preliminary Guide for Conformance with OSHA's Rule for Process Safety Management of Highly Hazardous Chemicals*, Draft, **DOE/EH**, Washington, DC, March 1993.

U.S. Department of Energy. *DOE Guideline: Guide for Chemical Process Hazard Analysis*, Draft, **DOE/EH**, Washington, DC, March 1993.

Westinghouse Hanford Company. *Operating Procedure: Chlorine Cylinder Handling and Storage*, **WHC-IP-384**, SW **U3-O-315-20**, **Richland**, WA, no date.

Zimmerman, **R.O.** Assessment of Chlorine Release From One-Ton Containers, **TC-** 1772, Hanford Engineering Development Laboratory, **Richland**, WA, 1980.